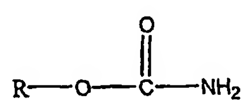
<u>Organic compounds</u>

This invention relates to tertiary carbamates and their use as fragrance ingredients. It furthermore relates to a method of making them and their use in fragrance compositions.

There is an ongoing need for powerful new perfumery ingredients which are stable towards aggressive media to which they are exposed. Surprisingly, we have found that certain tertiary non-vinylic carbamates, which have olfactory properties useful for perfumery, are stable against hydrolysis over a wide range of pH and towards oxidation. With the exception of *N*- or *O*- vinyl carbamates, tertiary carbamates constitute valuable ingredients for the perfumery industry. *O*- and *N*-vinyl carbamates, in analogy to enol esters and enamides, are susceptible to acid-catalyzed hydrolysis. Furthermore, in accordance with their use as monomers in the polymer industry, they polymerize easily. The aforementioned tertiary non-vinylic carbamates exhibit odours in the spicy, herbaceous or floral-rosy range with excellent substantivity and are useful as fragrance ingredients.

The use as fragrance ingredients of tertiary non-vinylic carbamates, i.e. non-vinylic carbamic acid ester of the formula



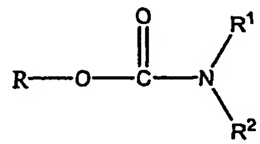
wherein the hydrogen atoms covalently bonded to the nitrogen atom are substituted, has not been previously described in the literature.

Thus, the present invention refers in a first aspect to the use as fragrance ingredients of tertiary non-vinylic carbamates, i.e. tertiary carbonates having no *N*-vinyl or *O*-vinyl substituent, having a molecular weight less than 350, preferably a molecular weight not higher than 300.

In a preferred embodiment, the present invention refers to the use as a fragrance ingredient of a *N,N*-substituted carbamate having a group covalently bonded to the ether oxygen atom of the carbamate, selected from the group consisting of alkyl, alk-(>1)-enyl, alkynyl, cycloalkyl, cycloalkenyl, phenyl, naphthyl, cycloalkylalkyl, cycloalkenylalkyl, phenylalkyl and naphtylalkyl, said covalently-bonded group being

optionally substituted with alkyl, alkenyl and alkoxy, and said group optionally comprising heteroatoms, for example oxygen, nitrogen or sulphur.

More particularly, the present invention refers to the use as fragrance ingredients of tertiary carbamates of formula (I)



wherein

R^1 and R^2 are independently selected from the group consisting of:

(a) C_1 to C_{11} alkyl, preferably C_1 to C_6 alkyl, e.g. methyl, ethyl, propyl, iso-propyl; C_3 to C_{11} alk-(>1)-enyl, preferably C_3 to C_6 alkenyl, e.g. prop-2-enyl; or C_2 to C_{11} alkynyl group; and

(b) cycloalkyl optionally substituted with alkyl, alkenyl and alkoxy group(s); C_3 to C_8 cycloalkenyl optionally substituted with alkyl, alkenyl and alkoxy group(s); or phenyl or naphthyl, wherein the aromatic ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); and

(c) C_4 to C_{14} cycloalkylalkyl, wherein the cycloalkyl ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); or phenylalkyl or naphthylalkyl, wherein the aromatic ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); and

R is selected from the group consisting of:

(a) C_1 to C_{11} alkyl; C_3 to C_{11} alk-(>1)-enyl; or C_2 to C_{11} alkynyl group; and

(b) cycloalkyl optionally substituted with alkyl, alkenyl, and alkoxy group(s); C_3 to C_8 cycloalkenyl optionally substituted with alkyl, alkenyl and alkoxy group(s); or phenyl or naphthyl optionally substituted with alkyl, alkenyl and alkoxy group(s); and

(c) C_4 to C_{14} cycloalkylalkyl, wherein the cycloalkyl ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); C_4 to C_{14} cycloalkenylalkyl, wherein the cycloalkenyl ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); or phenylalkyl or naphthylalkyl, wherein the aromatic ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); and

(d) C_5 to C_{14} cycloalkylalkoxyalkyl, wherein the cycloalkyl ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); C_5 to C_{14} cycloalkenylalkoxyalkyl, wherein the cycloalkenyl ring is optionally substituted

with alky, alkenyl and alkoxy group(s); or phenylalkoxyalkyl or naphthylalkoxyalkyl, wherein the aromatic ring is optionally substituted with alkyl, alkenyl and alkoxy group(s); and

(e) heteroaromatic ring, e.g. pyridyl, furyl; heteroarylalkyl ring, e.g. furylmethyl, pyridylmethyl, pyridylethyl; heterocyclic ring, e.g. dihydrofuryl, tetrahydrofuryl; or heterocycloalkyl ring, e.g. dihydrofurylmethyl, tetrahydrofurylmethyl, wherein the ring is optionally substituted with alkyl, alkenyl and alkoxy group(s), the ring having 5 to 6 ring members, and the hetero atom is oxygen or nitrogen; and

R, R^1 and R^2 having together 7 to 18 carbon atoms, more preferably 7 to 16 carbon atoms, most preferably 8 to 12; or

R^1 is selected from the group consisting of:

(a) C_1 to C_6 alkyl; C_3 to C_5 alk-(>1)-enyl; or C_2 to C_5 alkynyl group; and

(b) C_3 to C_6 cycloalkyl optionally substituted with alkyl and alkenyl group(s); C_3 to C_6 cycloalkenyl optionally substituted with alkyl and alkenyl group(s); or phenyl optionally substituted with alkyl and alkenyl group(s); and

(c) C_4 to C_8 cycloalkylalkyl, wherein the cycloalkyl ring is optionally substituted with alkyl and alkenyl group(s); or phenyl alkyl, wherein the aromatic ring is optionally substituted with alkyl and alkenyl group(s); and

R and R^2 form together with the atom to which they are attached a 5 to 8 membered heterocyclic ring, which is optionally substituted with alkyl and alkenyl group(s); and R, R^1 and R^2 having together 7 to 18 carbon atoms, more preferably 7 to 16 carbon atoms, most preferably 8 to 12.

As used in relation to compounds of formula (I) unless otherwise indicated "cycloalkyl" refers to C_3 to C_8, preferably C_4 to C_6, e.g. cyclopentyl, cyclohexyl; "alkyl" refers to linear or branched C_1 to C_5 alkyl, e.g. n-pentyl, sec-pentyl, tert-pentyl, n-butyl, sec-butyl, tert-butyl , preferably C_1 to C_3, e.g. methyl, ethyl, i-propyl; "alkenyl" refers to vinyl or linear or branched C_3 to C_5 alkenyl, e.g. propen-1-yl, propen-2-yl, allyl, and but-2-en-1-yl; "alk-(>1)-enyl" refers to C_3 to C_{11} linear or branched alkenyl in which there is at least one sp^3-hybridised C-atom between the *N*-atom or ether oxygen atom of the carbamate and the nearest C-C double bond, e.g. hex-3-en-1-yl, 3-methyl-but-2-en-1-yl; and "alkoxy" refers to C_1 to C_4, such as methoxy, ethoxy, and isopropoxy.

By the term "optionally substituted", as used in relation to compounds of formula (I) is meant that there is no substitutent, or there is at least one substituent, for example one or more alkyl group(s), one or more alkenyl group(s), or one or more alkoxy group(s), or a combination of at least two substituents, e.g. an alkyl group and an alkoxy group, two alkyl groups and one alkenyl group, one alkyl group and one alkenyl group.

Preferred are compounds according to formula (I), wherein R^1 and R^2 together have 2 to 13 carbon atoms, more preferably 2 to 9 carbon atoms, most preferably 2 to 6 carbon atoms. Compounds according to the present invention wherein R^1=R^2 are also preferred.

The compounds of formula (I) may comprise one or more chiral centres and as such may exist as a mixture of stereoisomers, or they may be resolved as isomerically pure forms. Resolving stereoisomers adds to the complexity of manufacture and purification of these compounds, and so it is preferred to use the compounds as mixtures of their stereoisomers simply for economic reasons. However, if it is desired to prepare individual stereoisomers, this may be achieved according to methods known in the art, e.g. preparative HPLC and GC or by stereoselective syntheses.

Whereas some compounds of the formula (I) have been described in the literature, others have not, and are novel.

Thus, in a second aspect of the invention, there is provided a compound of formula (I) wherein R, R^1 and R^2 are selected according to the following table:

R	R^1	R^2
hex-3-enyl	ethyl	ethyl
2-ethyl-hexyl	methyl	methyl
methyl	ethyl	methyl-tolyl
methyl	ethyl	ethyl-tolyl
3-methyl-but-2-enyl	ethyl	ethyl
3-methyl-but-3-enyl	ethyl	ethyl
hex-3-enyl	methyl	iso-propyl
2,2,5-trimethyl-hex-4-enyl	ethyl	ethyl
undec-10-enyl	methyl	methyl

2-ethyl-hexyl	methyl	iso-propyl
2-ethyl-hexyl	ethyl	iso-propyl
R and R^1 together with the atoms to which they are attached is 4-Methyl-oxazolidyl-2-one		pentyl
1,1-dimethyl-(4-methyl-cyclohex-3-enyl)-ethyl	methyl	methyl
1,1-dimethyl-(4-methyl-cyclohex-3-enyl)-methyl	methyl	methyl
ethyl	methyl	hexyl
2-methyl-propyl	methyl	butyl
2-methyl-propyl	ethyl	butyl
1,2-dimethyl-1-propyl-propyl	methyl	methyl
1,2-dimethyl-1-propyl-iso-propyl	methyl	methyl
2-ethoxy-phenyl	methyl	methyl
2-[1-(3,3-dimethyl-cyclohexyl)-ethoxy]-2-methyl-propyl	methyl	methyl
2-[1-(3,3-dimethyl-cyclohexyl)-ethoxy]-2-methyl-propyl	ethyl	ethyl
furylmethyl	ethyl	ethyl

The compounds according to the present invention may be used alone or in combination with known odourant molecules selected from the extensive range of natural and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles, and/or in admixture with one or more ingredients or excipients conventionally used in conjunction with odourants in fragrance compositions, for example, carrier materials, and other auxiliary agents commonly used in the art.

The following list comprises examples of known odourant molecules, which may be combined with the compounds of the present invention:

- ethereal oils and extracts, e.g. castoreum, costus root oil, oak moss absolute, geranium oil, jasmin absolute, patchouli oil, rose oil, sandalwood oil or ylang-ylang oil;

- alcohols, e.g. citronellol, Ebanol™, eugenol, geraniol, Super Muguet™, linalool, phenylethyl alcohol, Sandalore™, terpineol or Timberol™.

– aldehydes and ketones, e.g. α-amylcinnamaldehyd, Georgywood™, hydroxycitronellal, Iso E Super®, Isoraldeine®, Hedione®, maltol, methyl cedryl ketone, methylionone or vanillin;

– ether and acetals, e.g. Ambrox™, geranyl methyl ether, rose oxide or Spirambrene™.

– esters and lactones, e.g. benzyl acetate, cedryl actetate, γ-decalactone, Helvetolide®, γ-undecalactone or vetivenyl acetate.

– macrocycles, e.g. ambrettolide, ethylene brassylate or Exaltolide®.

– heterocycles, e.g. isobutylchinoline.

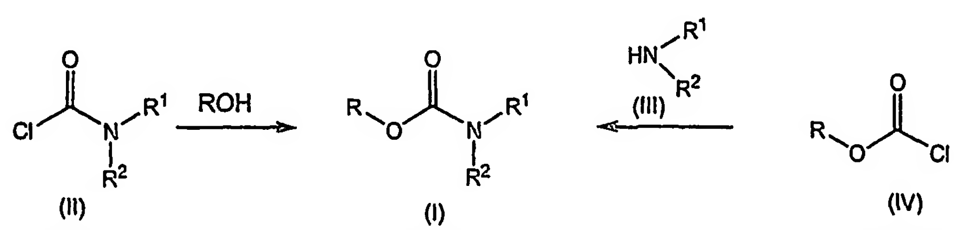
The compounds of the present invention may be used in a broad range of fragrance applications, e.g. in any field of fine and functional perfumery, such as perfumes, household products, laundry products, body care products and cosmetics. The compounds can be employed in widely varying amounts, depending upon the specific application and on the nature and quantity of other odourant ingredients. The proportion is typically from 0.001 to 20 weight percent of the application. In one embodiment, compounds of the present invention may be employed in a fabric softener in an amount of from 0.001 to 0.05 weight percent. In another embodiment, compounds of the present invention may be used in an alcoholic solution in amounts of from 0.1 to 20 weight percent, more preferably between 0.1 and 5 weight percent. However, these values are given only by way of example, since the experienced perfumer may also achieve effects or may create novel accords with lower or higher concentrations.

The compounds of the present invention may be employed into the fragrance application simply by directly mixing the fragrance composition with the fragrance application, or they may, in an earlier step be entrapped with an entrapment material such as for example polymers, capsules, microcapsules and nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, or they may be chemically bonded to substrates, which are adapted to release the fragrance molecule upon application of an external stimulus such as light, enzyme, or the like, and then mixed with the application.

Thus, the invention additionally provides a method of manufacturing a fragrance application, comprising the incorporation as a fragrance ingredient of a tertiary carbamate having a molecular weight less than 350.

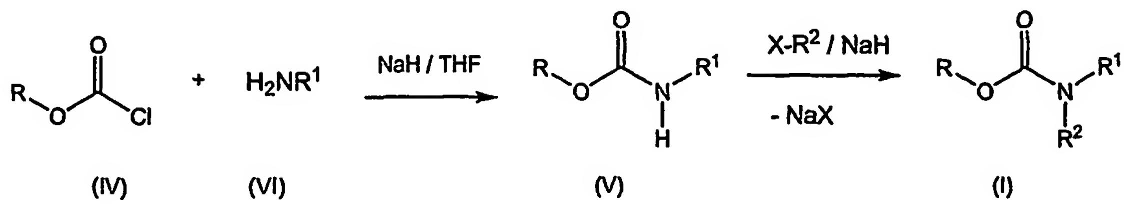
Linear *N,N*-dialkylcarbamate compounds of formula (I), i.e. compounds of formula (I) wherein R and R^2 together with the atoms to which they are attached do not form a ring, may be synthesised by reacting the corresponding chloroformic acid alkyl ester of formula (IV) e.g. chloroformic acid hex-3-enyl ester, with the corresponding dialkylamine of formula (III), e.g. diethylamine, or they may be synthesised by reacting the corresponding dialkyl carbamoyl chloride of formula (II), e.g. dimethyl carbamoyl chloride, with the corresponding alcohol ROH, e.g. 2,3,4-trimethyl-pentan-3-ol, as shown in Scheme 1. The appropriate method to use depends mainly on the availability of the starting materials. Other routes may also be used, for example, the reaction of an alcohol ROH with an *N*-alkylisocyanates, as known to a person skilled in the art, and described for example in DE 3312498.

Scheme 1:



Furthermore, linear *N,N*-dialkylcarbamate compounds of formula (I) may be synthesised by a two step process by reacting the corresponding primary amine, e.g. isopropylamine, with the corresponding chloroformic acid alkyl ester of formula (IV), e.g. chloroformic acid 2-ethyl hexyl ester, in the presence of one mole equivalent of a base, for example NaH, resulting in the corresponding secondary carbamate of formula (V) in a first step. Further alkylation of the secondary carbamate by adding the corresponding alkylating agent, e.g. alkyltoluene sulfonates, alkylmethane sulfonates, dialkyl sulfates (for example dimethyl sulfate), and alkyl halides, in the presence of one mole equivalent of a base, for example NaH, results in the corresponding linear *N,N*-dialkylcarbamate compounds of formula (I), as shown in Scheme 2.

Scheme 2



The process according to Scheme 2 is particularly useful for the production of non-symmetrical *N,N*-dialkylcarbamate compounds of formula (I), i.e. compounds according to the present invention wherein R^1 is different from R^2. Using the two-step process has the advantage that such non-symmetrical *N,N*-dialkylcarbamate compounds may be synthesised in one reaction vessel without isolating the intermediate.

Thus, a further aspect of the present invention is a process for the production of a compound of formula (I) by

(a) reacting a primary amine of formula (VI) in the presence of a base, e.g. NaH with a chloroformic acid alkyl ester of formula (IV) to give a secondary carbamate of formula (V), and then

(b) reacting the secondary carbamate of formula (V) in the presence of a base, e.g. NaH with an alkylating agent of the formula

R^2-X,

wherein X is Br^-, Cl^-, J^-, or $R^4\text{-}SO_4^-$, wherein R^4 is methyl or tolyl, and wherein R, R^1 and R^2 are as hereinabove defined, and step (a) and (b) are sequentially carried out in the same reaction vessel.

Cyclic carbamate compounds of formula (I), i.e. wherein R and R^2 together with the atoms to which they are attached form a ring, may be synthesised by reaction of dialkyl carbonate, e.g. diethyl carbonate and dimethyl carbonate, with the corresponding primary amino-alcohol, e.g. 2-aminopropanol, in the presence of alkali alcoholate, e.g. sodium ethanolate, followed by alkylation of the resulting secondary amine, which results in the cyclic tert. carbamate of formula (I). Cyclic carbamate compounds of

formula (I) may also be synthesised by ring-closing metathesis reaction of carbamate bridged diolefins as well known to the person skilled in the art.

The invention is now further described with reference to the following non-limiting examples.

Example 1: Diethyl-carbamic acid hex-3-enyl ester (Table 1, compound No1)

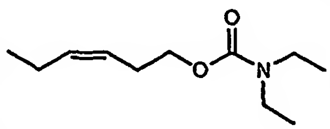
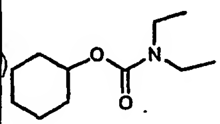
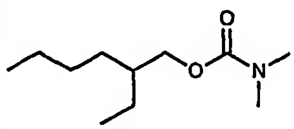
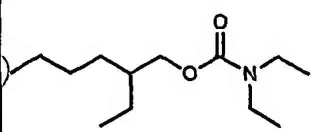
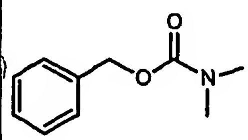
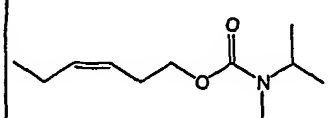
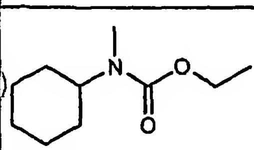
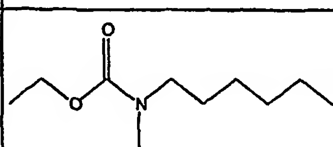
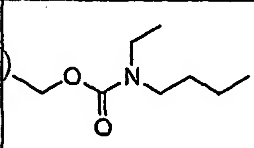
Diethylamine (9.1g, 125mmol, 1.25 equiv.) was added to a 2%-aqueous NaOH-solution (200ml) and the resulting mixture was cooled to 0°C (icebath). At this temperature chloroformic acid hex-3-enyl ester (16.2g, 100mmol) in diethyl ether (200ml) was added over a period of 35min. After complete addition, the cooling bath was removed and stirring was continued for 1.5h. The mixture was acidified with 2N aqueous HCl-solution, the phases separated and the organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified via fractionated distillation (74-76°C/0.05mbar) to yield 18.2g (92%) of product.

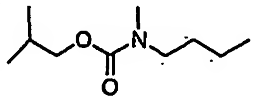
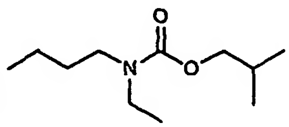
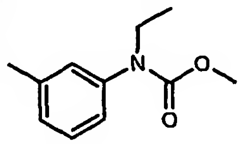
IR (film): 2967w, 1698vs, 1272s, 1171s, 1072m, 770m. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.50- 5.46 (m, 1H), 5.37-5.33 (m, 1H), 4.07 (t, J=7 2H), 3.30 (br. s, 4H), 2.39 (q, J=7, 2H), 2.07 (quint, J=7, 2H), 1.11 (t, J=7, 6H), 1.00 (t, J=8, 3H). ^{13}C-NMR: 155.9 (s), 133.9 (d), 124.2 (d), 64.4 (t), 41.5/41.1 (br. t, 2 rotamers), 27.1 (t), 20.4 (t), 14.1 (q), 13.8/13.4 (br. q, 2 rotamers). MS (EI 70 eV): 199 (<1%, M+), 118 (100), 100 (45, 82 (39), 72 (33), 67 (55), 55 (68).

Odor description: green, peppery, liquorice

Further compounds as listed in Table 1 were prepared according to the procedure described above.

Table 1:

No.	Structure	yield	^{13}C-NMR-data (400 MHz, $CDCl_3$)	MS *	Olfactory description
1		92%	155.9 (s), 133.9 (d), 124.2 (d), 64.4 (t), 41.5/41.1(br. t, 2 rotamers), 27.1 (t), 20.4 (t), 14.1 (q), 13.8/13.4 (br. q, 2 rotamers)	199	green, peppery, liquorice
2		57%	155.5 (s), 72.4 (d), 41.3 (br. t), 31.8 (d), 25.4 (d), 23.5 (d), 13.7 (br. q)	199	floral, minty, terpenyl acetate
3		92%	156.8 (s), 67.6 (t), 38.9 (d), 36.1/35.6 (br. q, 2 rotamers), 30.3 (t), 28.8 (t), 23.7 (t), 22.8 (t), 13.8 (q), 10.9 (q)	201	anisic, floral, spicy
4		78%	156.1 (s), 67.1 (t), 41.3 (br. t), 39.0 (d), 30.4 (t), 28.8 (t), 23.8 (t), 22.8 (t), 13.9 (q), 13.6 (br. q), 10.9 (q)	229	green, woody, spicy, vetyver, gaïac
5		25%	156.3 (s), 136.9 (s), 128.3 (d), 127.8 (d), 127.7 (d), 66.9 (t), 36.3/35.8 (br. q, 2 rotamers)	179	fruity, rosy
6		77%	156.0 (s), 134.0 (d), 124.1 (d), 64.5 (t), 46.2 (d), 27.1 (t), 20.4 (t), 19.6 (br. q), 14.1 (q)	199 (118)	peach, veloutone, nectaryl
7		70%	156.2(s), 60.8 (t), 54.5 (br. d), 30.1 (br. t), 28.0 (br. q), 25.6 (d), 25.4 (d), 14.6 (q)	185 (142)	mushroom, minty, herbal
8		71%	156.4 (s), 60.8 (t), 48.8/48.4 (br. t, 2 rotamers), 34.2/33.6 (br. q, 2 rotamers), 31.4 (t), 27.6/27.3(br. t, 2 rotamers), 26.1 (t), 22.4 (t), 14.6 (q), 13.8 (q)	187 (116)	floral, green, jasmin
9		57%	156.0 (s), 60.5 (t), 46.4/45.8 (br. t, 2 rotamers), 41.6/41.4 (br. t, 2 rotamers), 30.6/30.3 (br. t, 2 rotamers), 19.7 (t), 14.4 (q), 13.6 (q), 13.1 (br. q)	173 (130)	celery, jasmine

10		59%	156.5 (s), 71.2 (t), 48.5/48.3 (br. t, 2 rotamers), 34.3/33.6 (br. q, 2 rotamers), 30.0/29.5 (br. t, 2 rotamers), 27.9 (d), 19.7 (t), 19.0 (q), 13.7 (q)	187 (57)	floral, leather
11		49%	156.2 (s), 71.0 (t), 46.6/46.1 (br. t, 2 rotamers), 41.9/41.5 (br. t, 2 rotamers), 30.8/30.4 (br. t, 2 rotamers), 27.9 (d), 19.9 (t), 19.0 (q), 13.7 (q), 13.8/13.2 (br. q, 2 rotamers)	201 (57)	floral, fruity, medicinal, woody
13		30%	155.8 (s), 141.5 (s), 138.8 (s), 128.6 (d), 127.9 (d), 127.4 (d), 124.3 (d), 52.6 (q), 45.3 (t), 21.2 (q), 13.5 (q)	193	fruity, green, rosy

* : molecular ion; in parentheses: 100% signal

Example 2: Dimethyl-carbamic acid 1-isopropyl-1,2-dimethyl-propyl ester (Table 2, Compound 24)

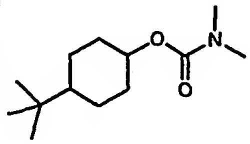
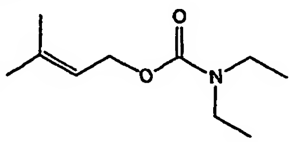
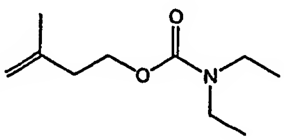
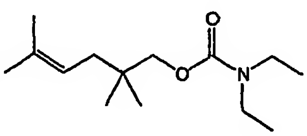
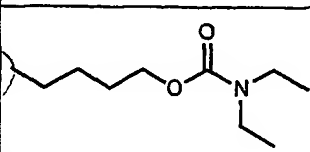
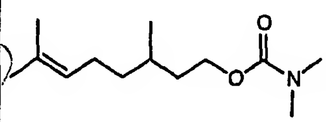
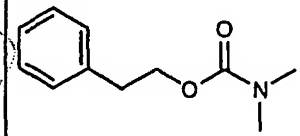
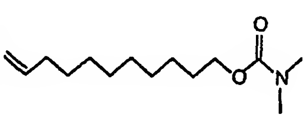
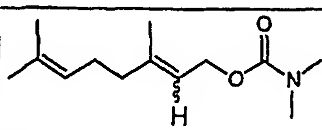
A solution of 2,3,4-Trimethyl-pentan-3-ol (13.0g, 100mmol, 1equiv.) in toluene (50ml) was added to a suspension of NaH (55% in mineral oil, 4.80g, 110mmol, 1.1equiv.) in toluene (50ml). The mixture was heated to 100°C for 1h, then cooled to 0°C. A solution of dimethyl carbamoyl chloride (12.9g, 120mmol, 1.2equiv.) in toluene (30ml) was added over 45min. The resulting suspension was stirred at room temperature for 19h, then diluted with MTBE and worked up as describe in Example 1. Distillation of the crude at 0.05mbar/52-61°C yielded 61% of product.

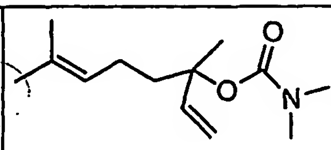
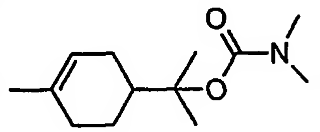
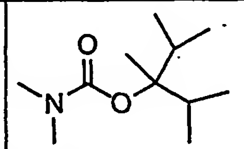
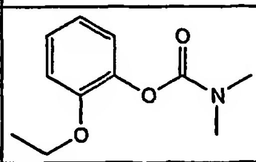
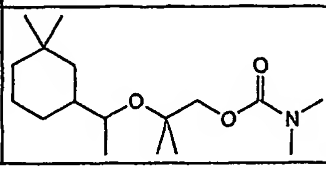
IR (film): 2967m, 1698vs, 1379s, 1196s, 868m, 769m. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.88 (br. s, 6H), 2.31 (hept, J=7, 2H), 1.41 (s, 3H), 0.97 (d, J=7, 6H), 0.94 (d, J=7, 6H). ^{13}C-NMR : 156.0 (s), 88.9 (s), 36.0 (q), 34.5 (d),18.3 (q), 18.1 (q), 17.9 (s). MS (EI 70 eV): 186 (<1%, $[M-1]^+$), 158 (4), 112 (37), 97 (67), 72 (71), 69 (72), 55 (100), 44 (83).

Odour description: fruity, rosy, spicy

Further compounds prepared following the synthesis protocol above were are listed in Table 2.

Table 2:

No.	Structure	yield	^{13}C-NMR-data (400 MHz, $CDCl_3$)	MS *	Olfactory description
12	 trans :cis = 3 :1	75%	(major trans diastereomer) 156.3 (s), 74.2 (d), 47.0 (d), 36.0/35.6 (br. q, 2 rotamers), 32.5 (t), 27.4 (d), 25.3 (t)	227	woody, fruity, vertenex type
14		37%	156.0 (s), 137.4 (s), 119.6 (d), 61.8 (t), 41.5/41.1 (br. t, 2 rotamers), 25.6 (q), 17.9 (q), 13.7/13.4 (br. q, 2 rotamers)	197	celery, spicy, animalic
15		83%	155.8 (s), 142.0 (s), 111.8 (d), 63.0 (t), 41.5/41.1 (br. q, 2 rotamers), 37.1 (t), 22.3 (q), 13.8/13.4 (br. q, 2 rotamers)	185 (102)	salicylate, quinoline, green, earthy
16		98%	156.0 (s), 133.4 (s), 120.1 (d), 72.8 (t), 41.6/41.1 (br. t, 2 rotamers), 37.2 (t), 35.0 (s), 25.9 (q), 24.1 (q), 17.6 (q), 14.0/13.4 (br. q, 2 rotamers)	124 (M-HCO_2NEt_2), (109)	fruity, rosy, spicy
17		75%	156.0 (s), 64.9 (t), 41.5/41.1 (br. t, 2 rotamers), 28.6 (t), 28.0 (t), 22.2 (t), 13.8 (q), 13.7/13.4 (br. q, 2 rotamers)	187 (43)	celery, jasminic
18		57%	156.7 (s), 131.0 (s), 124.5 (d), 63.7 (t), 36.8 (t), 36.2/35.6 (br. q, 2 rotamers), 35.8 (t), 29.3 (d), 25.5 (q), 25.2 (t), 19.3 (q), 17.5 (q)	227 (81)	rosy, pear, apricot
19		45%	156.4 (s), 138.1 (s), 128.8 (d), 128.3 (d), 126.4 (d), 65.7 (t), 36.2 (br. q), 35.6 (br. q), 35.5 (t)	193 (104)	balsamic, spicy, rosy
20		63%	156.7 (s), 139.0 (d), 114.0 (t), 65.3 (t), 36.2 (br. q), 35.6 (br. q), 33.6 (t), 29.3 (t), 29.2 (t), 29.1 (t), 28.9 (t), 28.8 (t), 25.8 (t)	241 (90)	green, orange blossom, rosy, woody
21	 E/Z=3:2	21%	(only E) 156.7 (s), 140.9 (s), 131.5 (s), 123.7 (d), 119.2 (d), 62.0 (t), 39.4 (t), 36.2/35.7 (br. q, 2 rotamers), 26.2 (t), 25.5 (q), 17.5 (q), 16.3 (q)	225 (69)	fruity, rosy

22		50%	155.3 (s), 142.7 (d), 131.4 (s), 123.9 (d), 112.3 (t), 81.8 (s), 40.2 (t), 35.9 (q), 25.5 (q), 23.8 (q), 22.3 (t), 17.4 (q)	225 (93)	woody, agarwood, olibanum, vetyver, peppery
23		50%	155.8(s), 133.7 (s), 120.4 (d), 83.4 (s), 43.2 (d), 35.9 (br. q), 30.8 (t), 26.3 (t), 23.9 (t), 23.5 (q), 23.5 (q), 23.2 (q)	210 (M-CH_3) (68)	fruity, gaïacwood
24		46%	156.0 (s), 88.9 (s), 36.0 (q), 34.5 (d),18.3 (q), 18.1 (q), 17.9 (s)	186 (M-CH_3) (55)	fruity, rosy, spicy
25		59%	154.8 (s), 150.8 (s), 141.0 (s), 126.0 (d), 123.1 (d), 120.5 (d), 113.5 (d), 64.2 (t), 36.6 (q), 36.4 (q), 14.7 (q)	209 (72)	spicy, eugenol, animalic, smokey
26		42%	156.4 (s), 77.2 (s), 71.5 (d), 71.0 (t), 42.1(t), 40.2 (d), 39.2(t), 36.2/35.7 (br. q, 2 rotamers), 33.5 (q), 30.5 (s), 28.1 (t), 24.5 (q), 24.1 (q), 22.1 (q), 19.7 (t), 19.6 (q)	197 (M-$C_4H_8NO_2$) (72)	musk

*: molecular ion; in parentheses: 100% signal

Example 3: Isopropyl-methyl-carbamic acid 2-ethyl-hexyl ester

A solution of isopropylamine (2.95g, 50mmol, 1equiv.) was added at RT to a suspension of NaH (55% in mineral oil, 2.40 g, 55 mmol, 1.1 equiv.) in THF (25ml). The mixture was warmed to 40°C for 18h, then chloroformic acid 2-ethyl-hexyl ester in THF (25ml) was added dropwise over 30min. After 4h further stirring a suspension of NaH (55% in mineral oil, 2.40g, 55mmol, 1.1equiv.) in THF (25 ml) was added followed by a solution of dimethyl sulfate (5.2ml, 55mmol, 1.1equiv.) in THF (20ml). The mixture was heated to 70°C for 16h, then hydrolysed by addition of water (50ml). The hydrolysed mixture was further heated to 70°C for 1.5h in order to destroy excess dimethyl sulfate, then diluted with MTBE and worked up as described in Example 1. The crude product was distilled at 0.06 mbar/94-95°C to yield 8.8 g (77%) of product.

IR (film) : 2960m, 2930m, 1697vs, 1323s, 1132s, 770m.
^{1}H-NMR (400 MHz, CDCl3) : 4.48- 4.20 (m, 1H), 4.00-3.92 (m, 2H), 2.74 (br. s, 3H), 1.58-1.56 (m, 1H), 1.40-1.25 (m, 8H), 1.10 (d, J=7, 6H), 0.92-0.88 (m, 6H).
^{13}C-NMR : see Table.
MS (EI 70 eV) : 229 (<1%, M^+), 214 (19), 118 (62), 102 (47), 71 (63), 58 (100).

Odour description: spicy, peppery

√ Example 4: 4-Methyl-3-pentyl-oxazolidin-2-one

4.1. 4-Methyl-oxazolidin-2-one (*cf.* K. Rein et al., *J. Am. Chem. Soc.* **1989**, *111*, 2211.)

Diethyl carbonate (46.8g, 397mmol, 1.2equiv.) was added to a catalytic amount (1mol%) of freshly prepared NaOEt (from 76mg Na and 0.4ml EtOH). 2-Aminopropanol (24.6g, 328mmol, 1equiv.) was then added and the resulting solution was heated to 125°C upon which EtOH started to distill. After 5h the mixture was cooled to room temperature and excess diethyl carbonate was removed in high vacuum 0.5mbar/50°C to give 33.0g (99%) of analytically pure 5-methyloxazolidinone as a pale yellow oil.

IR: 3290 br., 2975 w, 1738 vs, 1481 m, 1238 m, 1029 s, 935 m. ^{1}H-NMR (400 MHz, $CDCl_3$) : 7.02 (br. s, 1H), 4.50 (t, J=8.2, 1 H), 4.02 (hext, J=4.4, 1H), 3.93 (dd, J=8.4, 6.4, 1H), 1.28 (d, J=6.4, 3H). ^{13}C-NMR : 160.0 (s), 71.4 (t), 48.0 (d), 20.3 (q). MS (EI) : 101 (27, M+), 86 (100, $[M-CH_3]^+$).

4.2. 4-Methyl-3-pentyl-oxazolidin-2-one

4-Methyl-oxazolidin-2-one (18.0g, 178mmol) in THF (100ml) was added slowly via dropping funnel to a slurry of hexane-washed NaH (60% in mineral oil, 7.12g, 178mmol, 1.0 quiv.) in THF (400ml) upon which H_2-evolution was observed. Neat iodopentane (70.51g, 356mmol, 2.0equiv.) was added rapidly and the mixture stirred for 1h at room temperature, then heated to reflux for 60h. After cooling to 5°C, 2N H_2SO_4 (180ml) was slowly added. The mixture was extracted with MTBE and worked up as usual. Distillation over a Widmer-column at 115°C/0.08mbar afforded the product as a slightly yellow liquid (20.54g, 73%).

^{1}H-NMR (400 MHz, $CDCl_3$): 4.40 (t, J=8.2, 1 H), 3.89 (hext, J=4.4, 1H), 3.82 (dd, J=8.4, 6.4, 1H), 3.40-3.36 (m, 1H), 3.10-3.03 (m, 1H), 1.65-1.42 (m, 2 H), 1.39-1.22 (m 4H), 1.28 (d, J=6.4, 3H), 0.90 (t, J=7.2, 3H). ^{13}C-NMR: 157.9 (s), 68.7 (t), 50.6 (d), 41.4 (t), 28.7 (t), 26.9 (t), 22.1 (t), 18.0 (q), 13.8 (q).MS (EI): 171 (2, M^+), 156 (33), 142 (5), 114 (100, $[M-C_4H_9]^+$), 102 (10), 86 (15), 70 (52).

Odour description: celery, jasminic

Example 5: Preparation of a spicy-woody masculine fragrance

	Weight parts
Bergamote Ess.	10
Ethylene Brassylate	50
Cardamome Graines Ess.	1
Floralym	25
Galaxolide 50 PHT	250
Georgywood	5
Givescone	2
Grapefruit Ess	5
Javanol	1
Kephalis	50
Lavance Ess.	5
Linalool Synt.	30
Moxalone 50% TEC	30
Diethylphtalate	265
Poivre Noir Ess.	10
Rose Pure Ether MEF	1
Salicylate Benzyle	150
Velvione	10
Total :	900

Addition of 100 weight parts of Dimethylcarbamic acid 1,5-dimethyl-1-vinyl-hex-4-enyl ester (Table 2, compound 22) enhances the spicy-peppery aspect of the fragrance and gives it more overall lift.